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STUDY OF THIN FILM LARGE AREA
PHOTOVOLTAIC SOLAR ENERGY CONVERTER

Ninth Monthly Status Report
October 1, 1963 through October 31, 1963
Contract No. NAS7-203

1. PRODUCTION OF EVAPORATED FILMS

Eighteen evaporations (evaporations 65 through 82) were completed during October. The numbers and types of films are: 54 films on 1-inch x 2-inch glass substrates, 2 films on 4-inch x 4-inch copper foil substrates, 1 film on a 4-inch x 4-inch glass substrate, 21 small area films in groups of 4 or 9 on 4-inch x 4-inch duPont H-Film, 1 film on a 4-inch x 4-inch H-film substrate, and one attempt with a polystyrene substrate.

The films deposited on glass were standard films and most of them were processed into cells. Evaporations on copper foil yielded films that showed no open circuit voltage. The attempt to evaporate CdS onto polystyrene ended when the polystyrene softened. Adherence to H-Film appears to improve when the H-Film is lightly sandblasted before evaporation. Most evaporations will be made on H-Film substrates from now on.

2. PROCESSING OF PHOTOVOLTAIC CELLS

Table I lists the properties of the better cells processed during October. All these cells are on glass substrates and have efficiencies in excess of 1.5 percent except for cell 80H-1 which was on a 4-inch x 4-inch H-Film substrate and had an efficiency of 0.9 percent. This film was held in a metal frame. A number of cells were made with efficiencies less than 1.5 percent. These represent deviations from the standard procedure; for example, some films were used to study barrier formation parameters in a high temperature drying oven.

The improvement in rectification characteristics and the increase in average open circuit voltages may be attributed to improvements in use of the copper slurry.

TABLE I PROPERTIES OF CdS PHOTOVOLTAIC CELLS

Cell No.	O.C.V.,* volts	S.C.C., mA	V _{mp} , volts	I _{mp} , mA	Active Area, cm ²	Efficiency, percent	Fill Factor
65-6A	0.50	7.6	0.38	5.5	0.6	3.4	0.55
65-6B	0.48	12.0	0.35	8.4	1.0	3.0	0.51
65-6C	0.49	13.0	0.36	10.4	1.2	3.1	0.59
65-6D	0.51	3.7	0.38	2.8	0.3	3.1	0.57
65-6**	0.49	35.5	0.34	26.5	3.2	2.9	0.52
65-1	0.47	2.8	0.35	2.0	0.2	3.2	0.53
82-1	0.47	79.0	0.33	61.0	7.4	2.7	0.54
69-7	0.52	57.0	0.40	44.0	7.1	2.5	0.59
82-7	0.50	44.0	0.40	36.0	7.4	2.0	0.65
82-4	0.46	37.0	0.35	28.0	6.6	1.5	0.58
47-1	0.44	51.0	0.30	39.0	8.0	1.5	0.52
68-6	0.46	0.8	0.32	0.6	0.13	1.5	0.52
65-7	0.45	10.0	0.33	8.3	2.0	1.5	0.61
80H-1	0.46	63.0	0.35	53.0	21.6	0.9	0.64

* O.C. = open circuit voltage; S.C.C. = short circuit current; V_{mp}, I_{mp} = voltage and current respectively at maximum power point.

** Cell 65-6 was composed of cells 65-6A through 65-6D connected in parallel.

3. MEASUREMENTS

Determinations of voltage-current characteristics, resistivity and carrier concentration are made on a routine basis. In the past month, the deterioration of cells has been under study. As reported previously, cell efficiency decreases approximately exponentially with time. Various attempts have been made to stop, retard and reverse the deterioration. Keeping the cells in a dessicator retards the drop-off in efficiency but does not stop it. In an attempt to reverse the progress of deterioration, a few cells were carefully and gently heated. This increased their efficiency from about 0.5 percent to about 0.7 percent. Additional heating to increase recovery destroyed the barrier layers.

Two film cells having initial efficiencies greater than 2 percent were placed in a vacuum dessicator.* After three days the efficiencies had dropped

* The dessicator leaked, reaching atmospheric pressure overnight. It was re-evacuated each morning.

to 1.5%. This represents a much slower rate of deterioration than experienced with unevacuated dessicators. Another experiment is in progress wherein the dessicator is pumped continually.

A number of materials have been employed to encapsulate cells. So far, none of the sealants tried, e.g., Krylon and a silicon resin spray, have been successful. Other materials have been ordered and will be tried when they arrive.

Heretofore, water vapor absorbed on the barrier layer has been suspected as the chief cause of cell deterioration. It is, of course, possible that some other contaminant is responsible and a careful review of cell manufacture is now under way to determine if this might be the case.

4. ALTERNATE METHODS OF PRODUCING FILMS

Work on sintering and spraying CdS films has stopped. Efforts are now concentrated on producing a CdS mirror and altering the surface of H-film to improve adhesion of CdS.

Attempts to hot-press CdS onto H-Film substrates were unsuccessful and for the present will be discontinued.

Experiments on CdS mirrors are interesting. These are analogous to the PbS mirror work. Principal problems are: 1) achieving slow precipitation of CdS to allow grain growth during the formation of a continuous layer on the substrate, and 2) effective processing of the substrate surface to ensure adherence of the CdS. The question of precipitating dopants along with CdS will be deferred until later.

For slow precipitation of CdS, thiourea and complex cadmium compounds are employed. In some experiments, polyvinylalcohol was added to increase the viscosity of the solution and retard the reaction. Thiourea, $(\text{CH}_2)_2\text{CS}$, in aqueous solution releases S^{2-} very slowly. The complex Cd compounds are formed with ligands, chosen in consideration of their "instability constants," K . The values of K should not exceed the solubility product of CdS (2.6×10^{-29}), otherwise precipitation would not occur. It is customary to deal with the "stability" constant pK defined by $\text{pK} = \log 1/K$.

Since CdS is soluble in acids all reactions took place in solutions made alkaline with NH_4OH or NaOH (pH 11 to 12). All experiments were carried out

in test tubes which were carefully cleaned and flamed. Test strips of H-Film, 3/4-inch x 2-inch x 0.002-inch were sandblasted on one side, washed with detergent, rinsed in deionized water and then with acetone. Stock solutions of 0.2 molar thiourea and 0.2 molar cadmium acetate were prepared. For each experiment, the chosen ligand was added to the cadmium acetate and enough NH_4OH or NaOH added to adjust the pH to 11 or 12. The two solutions were poured together into a clean test tube containing a strip of H-Film. Usually, after 10 or 15 minutes, the mixture became opalescent, then acquired a yellow tint and, after several hours, particle aggregation would begin. The reaction rate could be increased by raising the temperature.

RESULTS:

1. Complex: $\text{Cd}(\text{NH}_3)_3^+$, $\text{pK} = 7.12$
Color of CdS: Orange.
Precipitate on H-Film: No adherence on either side.
Precipitate on test tube wall: Thin, strongly adhering.
2. Complex $\text{Cd}(\text{EDTA})^{++}$, $\text{pK} = 16.48$
Color of CdS: Lemon yellow.
Precipitate on test tube wall: Firmly adherent, thin. Results unchanged when polyvinylalcohol was added. Precipitate on H-Film: Adhered only on sanded side. Very thin.
3. Complex: $\text{Cd}(\text{CN})_4^{--}$, $\text{pK} = 18.85$
Color of CdS: Orange
Precipitate on H-Film: Flaky. Did not adhere.
Precipitate on test tube wall: Flaky. Did not adhere.
Results unchanged when polyvinylalcohol was added.

Experiments with other ligands and an investigation of the effects of strong alkalies on H-Film are in preparation.

5. SUMMARY AND PLANS FOR NEXT MONTH

CdS cells on glass substrates having areas of the order of 7 cm^2 and efficiencies between 2 and 2.5 percent are achieved without difficulty.

CdS on H-Film substrates exhibit lower efficiencies due, in part, to the

optical absorption of the H-Film. Future work will emphasize H-Film substrates. There is no reason to expect a significant difference between glass and H-Film substrates, so it is presumed that small adjustments to evaporation parameters will result in 2 percent efficiencies in the near future. Curling of the H-Film when CdS is evaporated on it remains a severe problem. A rough calculation of the tensile stress in the flattened CdS-H film composite based ^{on the} radius of curvature yields a value of 30×10^6 newtons/meter² (~5000 psi). Several methods of combating this curling are under consideration.

The "wet chemistry" approach to depositing a CdS mirror looks reasonably promising and will be pursued further in the next month.

Film structure studies are no longer a principal phase of this project. X-ray, electron microscope and electron diffraction measurements will be made only when necessary.

6. PERSONNEL

Time devoted to this project by principal technical personnel and others during the month of October follows:

Personnel	Man-hours
W. J. Deshotels	176
F. Augustine	184
J. Koenig	184
Others	<u>602</u>
Total	1146

7. EXPENDITURES

Actual costs to September 30, 1963	\$ 124,800
Estimated Costs for October 1963	\$ 10,270 .

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